

In situ Remediation of Sites Contaminated with Organic Compounds Using Iron-Catalyzed Persulfate as an Oxidant

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Abstract

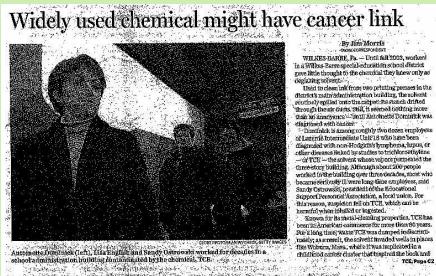
In situ chemical oxidation (ISCO) technologies have been used for degradation of organic compounds in soil and groundwater at hazardous waste sites. However, some commonly used oxidants, such as the Fenton's reagent and permanganates, have limitations for ISCO applications and therefore cannot be universally applied. Chemical oxidation using iron-catalyzed persulfate (ICP) results in the formation of a highly reactive sulfate free radical. Use of ICP potentially represents an innovative technology for the *in situ* treatment of soils and groundwaters contaminated with organic compounds, including chlorinated solvents such as trichloroethylene (TCE).

The objective of the proposed laboratory-scale study is to determine the full range of capabilities and limitations of the use of ICP for the destruction of TCE in soil and groundwater. Experiments are being conducted on select contaminant to study interactions between the contaminant, oxidant, ferrous and ferric forms of iron, and a chelating agent. Aqueous samples of the target contaminant were prepared in the laboratory. Experiments were conducted in the laboratory under controlled conditions. Analysis of contaminants in the aqueous medium was conducted in accordance with appropriate U.S. Environmental Protection Agency (U.S. EPA) methods. Iron, pH, persulfate ion, chelating agent, and target contaminants were monitored during the experiments. Based on preliminary experiments conducted at the UMASS Lowell Civil & Environmental Engineering Laboratory, ICP appears to be a superior ISCO oxidant due its persistence potential. Based on results from limited experiments, it appears that ferric iron in the presence of the chelant forms ferrous ions that activate the formation of sulfate free radicals. These sulfate free radicals are then able to degrade the target organic contaminants. In the natural environment (i.e., soil and groundwater) iron is generally found in the ferric form. The experimental results suggest that native iron from sites, if available at appropriate levels, may be utilized to catalyze the oxidation reactions. Additional experiments are being carried out jointly at the Civil & Environmental laboratory at UMASS Lowell and at the U.S. EPA's New England laboratory in North Chelmsford, MA.

Background

The Boston Globe

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- Trichloroethylene (TCE) is a commonly used industrial degreasing agent that is reported to be carcinogenic to humans
- TCE is found in soil and groundwater at hazardous waste sites due to accidental releases
- Up to 300,000 lbs. of TCE were released to water and land in U.S. between 1987-1993
- The EPA maximum contaminant level for TCE in drinking water is 5 µg/L

In situ chemical oxidation (ISCO)

Advantages

- In-situ destruction of contaminants
- Potential to oxidize TCE to "harmless bi-products"
- Fast treatment (within weeks)
- Potential for other remediation techniques to complement ISCO for cost optimization
- Potential to meet regulatory standards at a disposal site

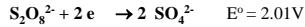
Issues

- Medium heterogeneity
- Understanding and monitoring subsurface geochemistry & interactions of oxidant(s) with medium
- Providing adequate contact (between oxidant and contamination zone) for the oxidation/ reduction reactions
- Monitoring for reaction bi-products and treatment effectiveness

Selected Oxidant for Research

Sodium Persulfate

- At ambient groundwater temperatures (12-15°C), the persulfate anion ($\text{S}_2\text{O}_8^{2-}$) is a strong two-electron oxidizing agent with a reduction potential of 2.01V



- In the presence of heat or divalent metal ions such as Fe^{2+} , $\text{S}_2\text{O}_8^{2-}$ forms highly reactive sulfate free radicals ($\text{SO}_4^{\cdot -}$) which have a reduction potential of 2.6 V:

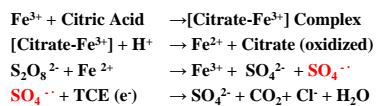


- Persulfate is relatively stable in groundwater and may persist for months.

Application of Oxidant



When persulfate is applied with a chelant (citric acid) and ferric iron, the following reactions occur resulting in degradation of TCE:



Analytical Methods & Instrumentation



- TCE is analyzed with a HP Model 5890 Gas Chromatograph using a Flame Ionization Detector
- Citric Acid is analyzed with a Waters Delta 600 HPLC Pump & Controller using a UV detector at 210 nm
- Ferrous and Ferric Iron are analyzed by the 1,10-Phenanthroline method with Hach DR/2000 spectrophotometer (Standard Methods) at a wavelength of 510 nm
- Persulfate is measured by an iodometric titration with thiosulfate (Kolthoff & Stenger)

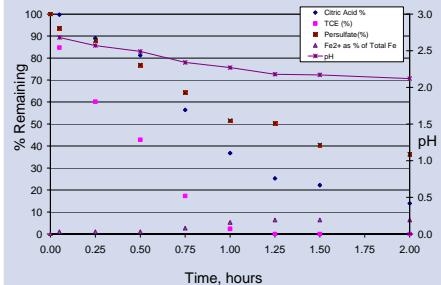
Selected Results & Conclusion

- Use of persulfates as an oxidant with chelated ferric iron as an activator appears to be a viable technology for *time-critical* remediation of TCE contaminated sites.
- In the presence of citric acid and ferric iron, ferrous iron is formed which in turn produces the sulfate free radicals in the presence of persulfate anion.
- The TCE degradation rate appears to be proportional to the ferric iron content.

% TCE, S_2O_8 , Citric Acid, Fe^{2+} Remaining & pH vs. Time

Molar Ratio of Persulfate:CA: Fe^{3+} :TCE = 19:1.9:1.9:1

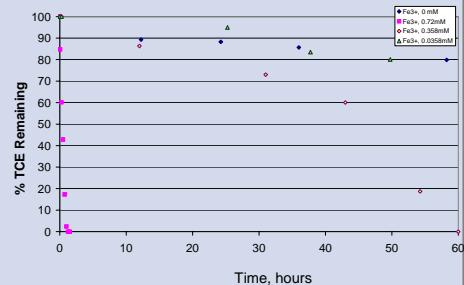
Temperature = 21.8°C



Rate of TCE Degradation with Changes in Iron(III) Concentration

TCE=0.4mM, Citric Acid=0.72mM, S_2O_8 =7.16 mM

Temp=20°C



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